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What's in a name?* 'Coinage-metal' non-covalent bonds and their definition

Anthony C. Legon^a and Nicholas R. Walker^b

Abstract.

Many complexes of the type $B \cdots MX$, (where B is a Lewis base such as H_2 , N_2 , ethyne, ethene, cyclopropane, H_2O , H_2S , PH_3 , or NH_3 , M is a coinage-metal atom Cu, Ag or Au, and X is a halogen atom) have now been characterised in the gas phase through their rotational spectra. It is pointed out that, for a given B, such complexes have angular geometries that are isomorphous with those of their hydrogen- and halogen-bonded counterparts $B \cdots HX$ and $B \cdots XY$, respectively. Since the MX are, like the B, HX and XY referred to, closed-shell molecules, the complexes $B \cdots MX$ also involve a non-covalent bond. Therefore, the name 'coinage-metal' bond is suggested for the non-covalent interaction in $B \cdots MX$, by analogy with hydrogen and halogen bonds. A generalised definition that covers all non-covalent bonds is also presented

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*"What's in a name? that which we call a rose

By any other name would smell as sweet."

W. Shakespeare, *Romeo and Juliet*, Act 2, Scene 2 (1597).

1. Introduction

There has been a rapid growth of literature concerned with non-covalent interactions in the last decade. IUPAC definitions of the hydrogen bond¹ and the halogen bond² have been established. An IUPAC Working Party is currently considering definitions of tetrel bonds, pnictogen bonds and chalcogen bonds.³ The number of recognised, named and defined non-covalent bonds is evidently increasing.

From the year 2000, the late Michael Gerry and co-workers observed the microwave spectra of many binary complexes of the type $\text{Rg}\cdots\text{M}-\text{X}$, where Rg is a rare gas atom, M is a group 11 transition metal atom (Cu, Ag, or Au) and X is a halogen atom (F, Cl, or Br).⁴⁻¹⁴ These molecules were produced by laser ablation of a rod of metal M in the presence of a pulse of the rare gas Rg containing a small amount of suitable X atom precursor (*e.g.* SF_6 , Cl_2 or Br_2). Interpretation of rotational spectroscopic constants of various isotopologues of $\text{Rg}\cdots\text{M}-\text{X}$ unambiguously characterised these linear molecules in some detail. Several molecules $\text{OC}\cdots\text{M}-\text{X}$ were soon identified¹⁵⁻¹⁷ and characterised in the gas-phase by similar methods. More recently, a whole family of related complexes $\text{B}\cdots\text{M}-\text{X}$, where B is a simple Lewis base, *e.g.* N_2 , ethyne, ethene, cyclopropane, H_2O , H_2S , PH_3 , or NH_3 and $\text{X} = \text{F}$, Cl or I have been identified by means of their rotational spectra, as observed by the laser-ablation method coupled with either a pulsed jet, F-T cavity microwave spectrometer or a chirped-pulse, broadband F-T microwave instrument.¹⁸⁻³⁸ Even examples where H_2 acts as the Lewis base have been investigated.^{39,40} Interpretations of observed rotational constants, centrifugal distortion constants and nuclear quadrupole coupling constants allowed these new molecules to be characterised in detail, including their radial and angular geometries.

2. Isomorphism among complexes involving non-covalent bonds

It was soon apparent that for a given B, the complexes $\text{B}\cdots\text{M}-\text{X}$ were isomorphous with those of the corresponding hydrogen-bonded complexes $\text{B}\cdots\text{HX}$ and halogen-bonded complexes $\text{B}\cdots\text{XY}$, where Y is also a halogen atom. This isomorphism can be readily identified in Figures 1 and 2, which compare the experimentally determined angular geometries of $\text{B}\cdots\text{CuCl}$ and $\text{B}\cdots\text{AgCl}$, with those $\text{B}\cdots\text{HCl}$ ^{41,42} and $\text{B}\cdots\text{ClF}$,^{43,44} for $\text{B} = \text{H}_2\text{O}$ and H_2S , respectively. The angular geometries were determined from zero-point spectroscopic constants and are therefore of r_0 type.

All H₂S complexes were shown to have a rigidly pyramidal (non-inverting), approximately right-angled arrangement at S ($\phi \sim 80\text{-}90^\circ$), while all H₂O analogues have an approximately tetrahedral configuration at O ($\phi \sim 40\text{-}50^\circ$) which undergoes rapid inversion, even in the zero-point state. *Ab initio* calculations at various levels of theory^{23,25,41,43,45} confirmed these conclusions (see the captions to Figures 1 and 2). Figure 3 shows schematic diagrams of H₂O and H₂S with non-bonding pairs illustrated in the exaggerated manner commonly used by chemists.

The angular geometries of B...HCl, B...ClF, B...CuCl and B...AgCl, when the Lewis bases B carry no n pairs of electrons but have either π pairs or pseudo- π pairs acting as the nucleophilic region, are shown in Figures 4, 5 and 6 for B = ethyne,^{29,30,46,47} ethene^{26,30,48,49} or cyclopropane,^{34,50,51} respectively. A schematic diagram for each of these Lewis bases is included in Figure 3 and shows the π electron density (for ethene and ethyne) or the pseudo- π electron density (for cyclopropane, as described by the Coulson-Moffitt model⁵²). The isomorphism among the angular geometries shown within each figure is again apparent. There is some distortion of the Lewis base for B = ethyne, ethene and cyclopropane on complex formation with either CuCl or AgCl, as discussed in detail in refs. 26,29,30 and 34. This distortion is more evident with CuCl because the interaction is stronger (see below). The geometries of the Lewis bases were assumed unchanged on complexation with HCl or ClF because the hydrogen and halogen bonds involved are much weaker than for MCl complexes. Subsequent *ab initio* calculations⁴⁵ confirmed negligible distortion in these cases. The remaining Lewis bases listed earlier form complexes with MCl, HCl or ClF that are either linear (N₂, CO) or have C_{3v} symmetry (PH₃, NH₃).

Evidently, the following simple rules, originally enunciated for complexes B...HX⁵³ and later extended to include the halogen-bonded species B...XY,⁵⁴ can also be used for B...M-X:

The angular geometries of non-covalent bonded complexes B...HX or B...XY or B...MX in the gas phase can be predicted by assuming that in the equilibrium conformation the internuclear axis of the HX or XY or MX molecule lies:

- (1) along the axis of a non-bonding electron pair (n-pair) carried by B, or
- (2) along the local symmetry axis of a π orbital, if B carries no n-pairs, or
- (3) if B carries both n- and π -pairs, rule 1 takes precedence.

The B...MX series of molecules tend to be more strongly bound (whether measured by the equilibrium dissociation energy D_e for the reaction $B \cdots MX = B + MX$ or by the intermolecular stretching quadratic force constant k_σ). Typical values are $D_e = \sim 50\text{-}100 \text{ kJ mol}^{-1}$ compared with $\sim 10\text{-}20 \text{ kJ mol}^{-1}$ for both hydrogen- and halogen-bonded analogues, and correspondingly $k_\sigma = \sim 100 \text{ N m}^{-1}$ and $\sim 10 \text{ N m}^{-1}$, respectively). It is now generally acknowledged that the predominant interaction in defining angular geometries for hydrogen- and halogen-bonded complexes is of the simple electrostatic type. Both CuCl and AgCl, for example, have large electric dipole moments [5.74 D^{55} and $6.076(60) \text{ D}^{56}$, respectively], compared with those of HCl [$(0.8881(2) \text{ D})^{57}$] and ClF [$(1.1086(3) \text{ D})^{58}$]. CuCl and AgCl also have large ionicities i_c , where ionicity, as calculated from chlorine nuclear quadrupole coupling constants,^{4,59} is a measure of the fractional contribution of the structure M^+Cl^- to the valence-bond description of the molecule. The i_c values for $^{63}\text{Cu}^{35}\text{Cl}$ and $^{107}\text{Ag}^{35}\text{Cl}$ are 0.71 and 0.67, respectively. The greater binding strength of members of the B...MCl series is then understandable in terms of the greater net positive charge, and therefore the greater electrophilicity, of the M atom in MCl compared with that of H in HCl or Cl in ClF. This enhanced polarity and electrophilicity of MX is evident from the molecular electrostatic surface potentials (MESPs) shown in Figure 7. The MESP is the potential energy of a non-perturbing, unit point positive charge, referred to an isosurface on which the electron density is constant (described as $0.00n \text{ e/bohr}^3$, see captions to figures for values of n). MESPs were calculated with the Spartan electronic structure package⁶⁰ at the M06/6-31G (D) level of theory for CuCl, M06/6-31G & LANL2DZ for AgCl, but M06/6-311G++** for ClF and HCl. The most electrophilic (deep blue, positive) region is more extensive in the MCl than in either HCl or ClF. These regions in MESP diagrams are commonly associated with the name σ -hole.^{61,62}

Figure 8 shows the MESPs similarly calculated for H_2S , H_2O , ethyne, ethene and cyclopropane. (M06/6-311G++** level). Two regions of most negative potential (red) in H_2S at approximately 90° to each other on the S atom are clearly observable and represent preferred sites/directions for the interaction of H_2S with the electrophilic end of MCl, HCl or ClF, in agreement with experimental angular geometries shown Figure 2. These regions of maximum negative potential can be identified with the two non-bonding electron pairs on S, which are at $\sim \pm 90^\circ$ to the H_2S plane and might be described roughly as occupying sp-hybrid orbitals. For H_2O , the (red) region of most negative potential in the MESP is not fully resolved into two distinct n-

pairs, an observation consistent with the approximately tetrahedral configuration at O in the various H₂O complexes shown in Figure 1 and with the facile inversion observed in the zero-point state in each case. The regions of π or pseudo- π electrons in ethyne, ethene and cyclopropane are obvious in Figure 8. It is also clear from Figure 8 that Rule 1 or 2 will be obeyed when the electrophilic end of MCl, HCl or ClF approaches the Lewis bases listed. Rule 3 has yet to be tested for B...MCl complexes.

3. Conclusions

The coinage/noble metal halides MX are, like the hydrogen halides HX and dihalogens XY, closed electron-shell diatomic molecules, as are all the Lewis bases B employed in the B...HX, B...XY and B...MX series discussed here. If a non-covalent interaction is defined as one involving the interaction of an electrophilic region of one closed-shell molecule with a nucleophilic region of another closed-shell molecule, then it follows that the complexes B...MX also involve such an interaction. The definition of the halogen-bond² is brief and, as pointed out first by Resnati and co-workers⁶³ and independently later,⁶⁴ can be readily adapted to include tetrel, pnictogen and chalcogen bonds. It can also encompass B...MX molecules, but first we need a name for the non-covalent interaction involved. By analogy with the term ‘halogen bond’, we might refer to it as a ‘coinage- (or noble-) metal’ bond.[†] Then a definition that covers coinage-metal bonds, tetrel bonds, pnictogen bonds, chalcogen bonds, halogen bonds (and even hydrogen bonds) is as follows:

An E bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with an E atom in a molecular entity and a nucleophilic region (e.g. a n-pair or π -pair of electrons) in another, or the same, molecular entity, where E is the name of an element of Group 1, 11, 14, 15, 16 or 17 in the Periodic Table.

Thus, E could be hydrogen, lithium, carbon, silicon, nitrogen, phosphorus, sulfur, bromine, etc., and we could refer to hydrogen bonds, lithium bonds (as first identified by Ault and Pimentel⁶⁵), carbon bonds,⁶⁶ and so on. This definition has an attractive generality, with the distinct advantage

[†]This nomenclature was anticipated in ref. 21 by the statement in its conclusion: ‘Nevertheless, it is clear that the geometries of H₂O...AgCl and H₂S...AgCl are isomorphic with those of their hydrogen- and halogen-bonded counterparts. Is there a silver bond analogous to the more familiar hydrogen and halogen bonds?’

that it can be applied to any other non-covalent interaction (as defined earlier, but recognising that non-covalent interactions involving open-shell species can also occur⁶⁷) subsequently identified or postulated. However, this definition requires the use of a different name for each non-covalent interaction when an atom of a different element E acts as the electrophilic region. We might avoid such a proliferation of named, non-covalent bonds by means of the following (slightly modified) definition in terms of the number of the group g of the Periodic Table in which the element $E\{g\}$ appears:

A group g non-covalent bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with an atom of an element $E\{g\}$ in a molecular entity and a nucleophilic region (e.g. a n -pair or π -pair of electrons) in another, or the same, molecular entity, where $E\{g\}$ is an element of Group g in the Periodic Table.

In general, if we define a molecule containing an electrophilic region associated with an atom of an element $E\{g\}$ belonging to Group g in the Periodic Table as $R-E\{g\}$, where R is the remainder of the molecule, then the non-covalent interaction of $R-E\{g\}$ with the nucleophilic region of a Lewis base molecule B is written as $B\cdots E\{g\}-R$. Thus, when $g = 1, 11, 14, 15, 16$ or 17 , for example, the non-covalent interaction (\cdots) in $B\cdots E\{g\}-R$ is described as an alkali-metal bond, a coinage-metal bond, a tetrel bond, a pnictogen bond, a chalcogen bond or a halogen bond, respectively.

We could generalise this even further and avoid the adjectives alkali-metal, coinage-metal, tetrel, pnictogen, chalcogen, etc. in the names of the bond and instead refer to g -N-C bonds, where $g = 1, 11, 14, 15, 16$, etc. and N-C means non-covalent. For example, an 11-N-C bond corresponds to a coinage-metal bond. But the names in words are probably already too firmly embedded in the literature, especially hydrogen bonds and halogen bonds, for such a proposal to be readily and broadly embraced. The fact that the hydrogen bond occurs in the alkali-metal bond grouping ($g = 1$) in the modified definition emphasises the uniqueness of this most common of all non-covalent interactions and provides good reason for retaining its familiar name.

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FIGURES

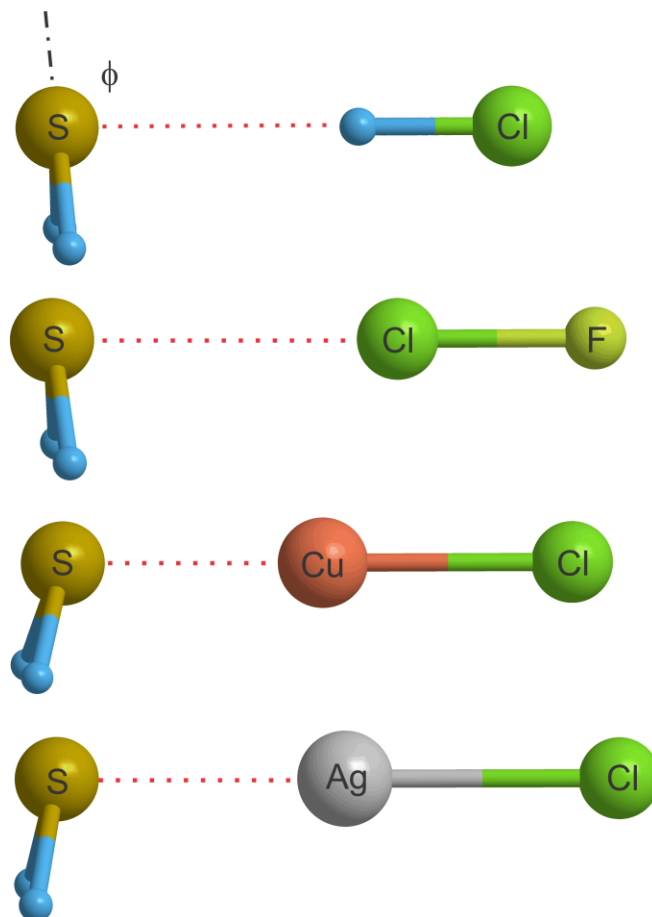


Figure 1. Angular geometries^{21, 25,42,44} of complexes $\text{H}_2\text{S}\cdots\text{HCl}$, $\text{H}_2\text{S}\cdots\text{ClF}$, $\text{H}_2\text{S}\cdots\text{CuCl}$ and $\text{H}_2\text{S}\cdots\text{AgCl}$, for which the angle $\phi/^\circ = 93.8(4)$ [84.9], 95.8(4) [85.0], 74.5(1) [73.4] and 78.7 [76.2], respectively. The ϕ in square brackets are equilibrium values from *ab initio* calculations (see text). The pyramidal configuration is in each case non-inverting on the timescale of microwave spectroscopy.

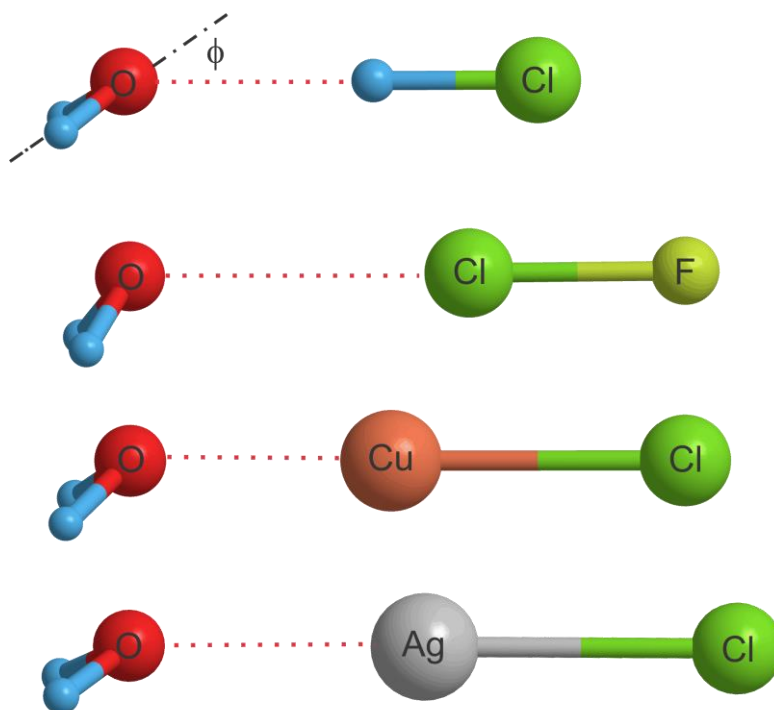


Figure 2. Angular geometries^{21,23,41,43} of complexes $\text{H}_2\text{O}\cdots\text{HCl}$, $\text{H}_2\text{O}\cdots\text{ClF}$, $\text{H}_2\text{O}\cdots\text{CuCl}$ and $\text{H}_2\text{O}\cdots\text{AgCl}$, for which the angle $\phi/^\circ = 37.4(4)$ [46.0], 58.9(16) [55.8], 40.9(13) [46.4] and 37.4(16) [43.7], respectively. The ϕ in square brackets are equilibrium values from *ab initio* calculations (see text). The reason why zero-point estimates of ϕ are systematically smaller than equilibrium values is discussed in ref. 41. In each case, the pyramidal configuration at O is rapidly inverting on the timescale of microwave spectroscopy, with $\text{H}_2\text{O}\cdots\text{ClF}$ having the smallest inversion frequency, the highest potential energy barrier and an angle nearest to the tetrahedral value.

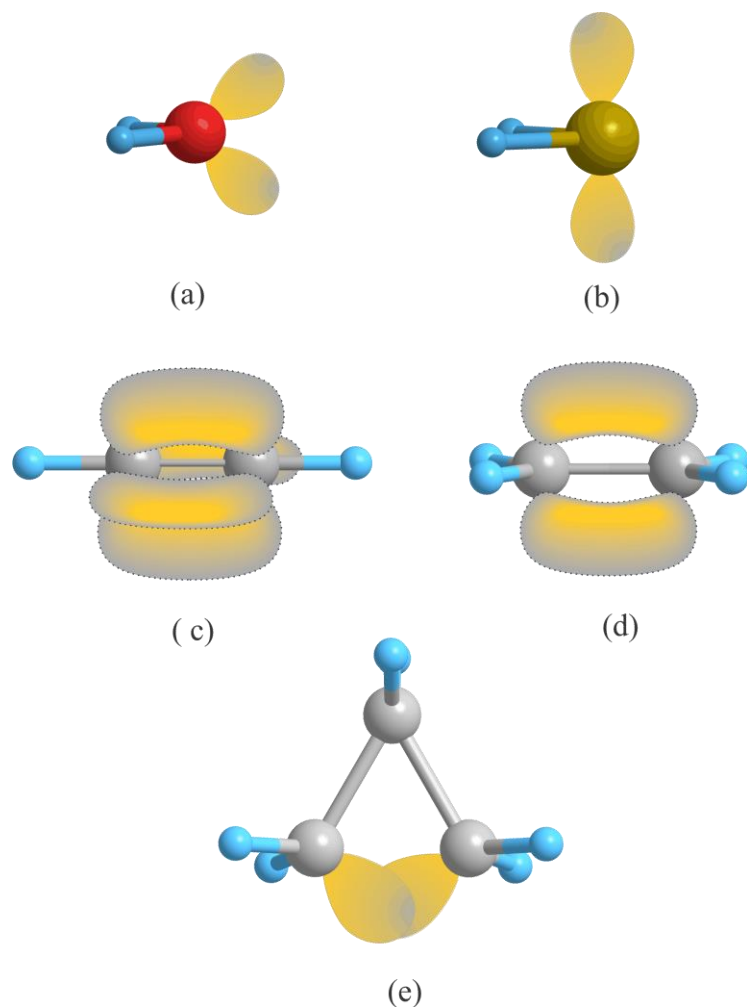


Figure 3. Schematic diagrams of (a) H₂O, (b) H₂S, (c) ethyne, (d) ethene and (e) cyclopropane showing the form of the n- pair or π -electron density distributions commonly used by chemists. In the case of cyclopropane, the Coulson-Moffitt model is employed, in which pseudo- π electron density is envisaged as formed by overlap of two sp^3 hybrid orbitals on adjacent carbon atoms to give a bent bond.

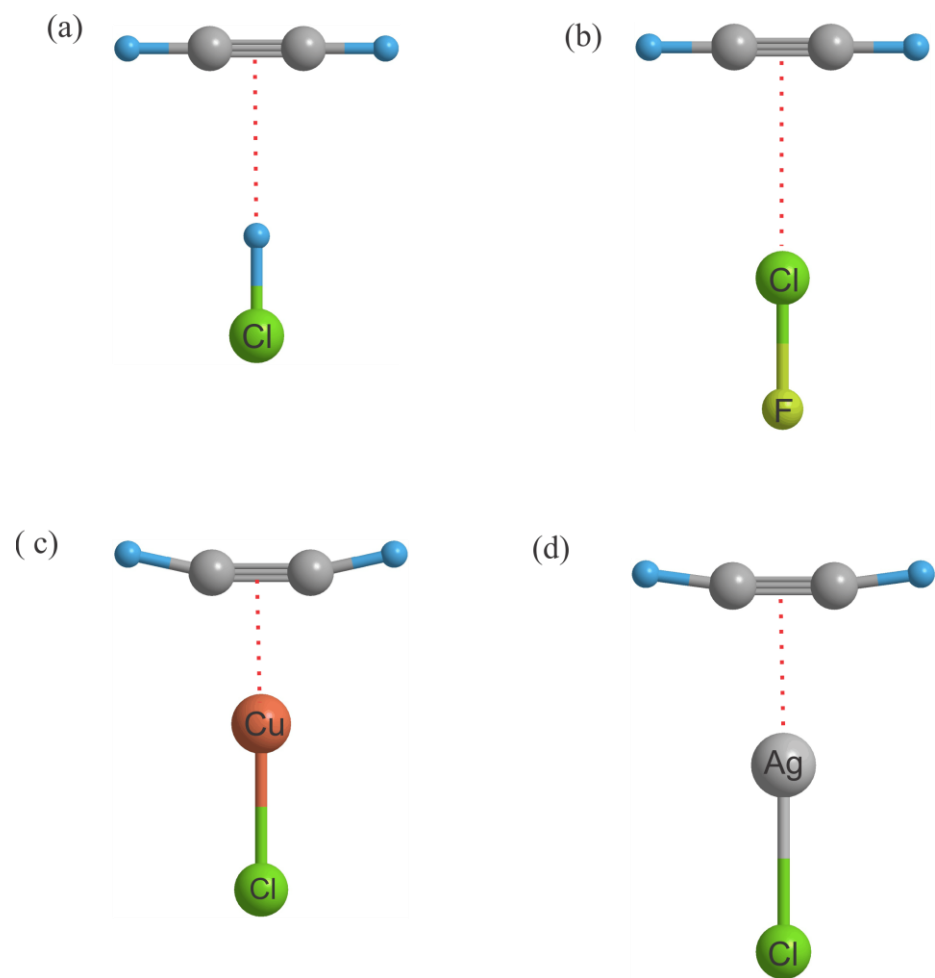


Figure 4. (a) -(d) Observed geometries of C₂H₂...HCl, C₂H₂...ClF, C₂H₂...CuCl and C₂H₂...AgCl, respectively, drawn to scale.

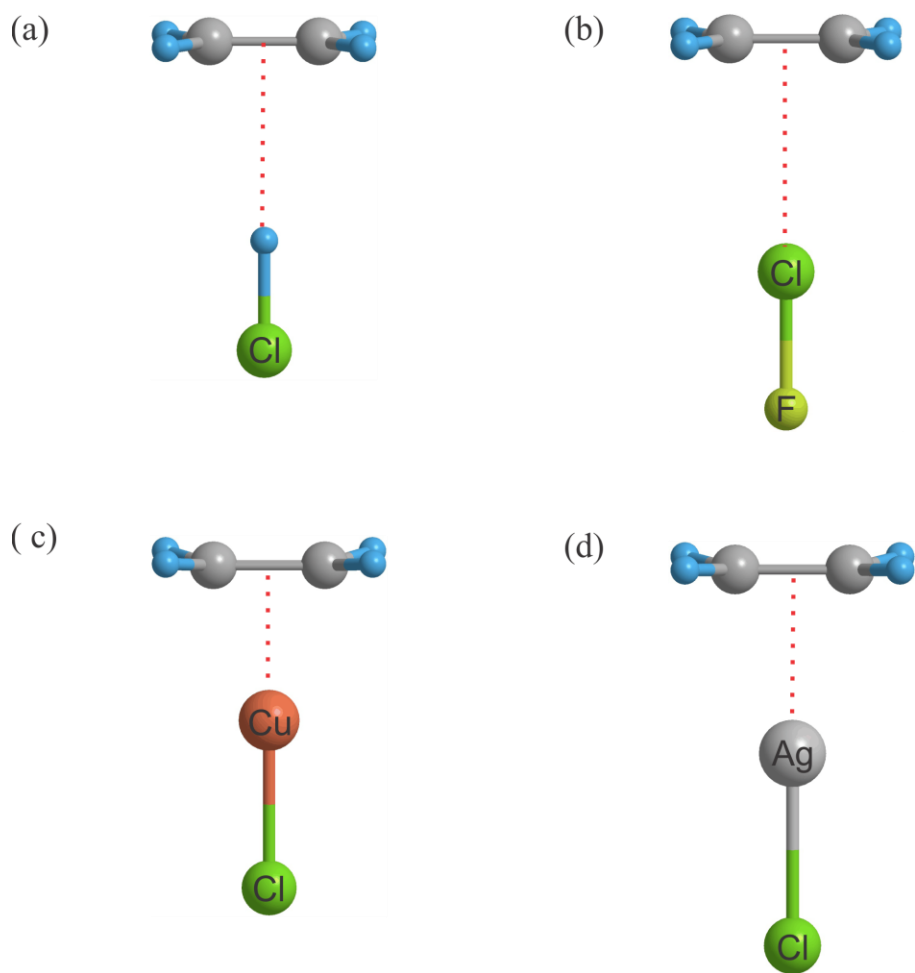


Figure 5. (a) -(d) Observed geometries of $\text{C}_2\text{H}_4 \cdots \text{HCl}$, $\text{C}_2\text{H}_4 \cdots \text{ClF}$, $\text{C}_2\text{H}_4 \cdots \text{CuCl}$ and $\text{C}_2\text{H}_4 \cdots \text{AgCl}$, respectively, drawn to scale.

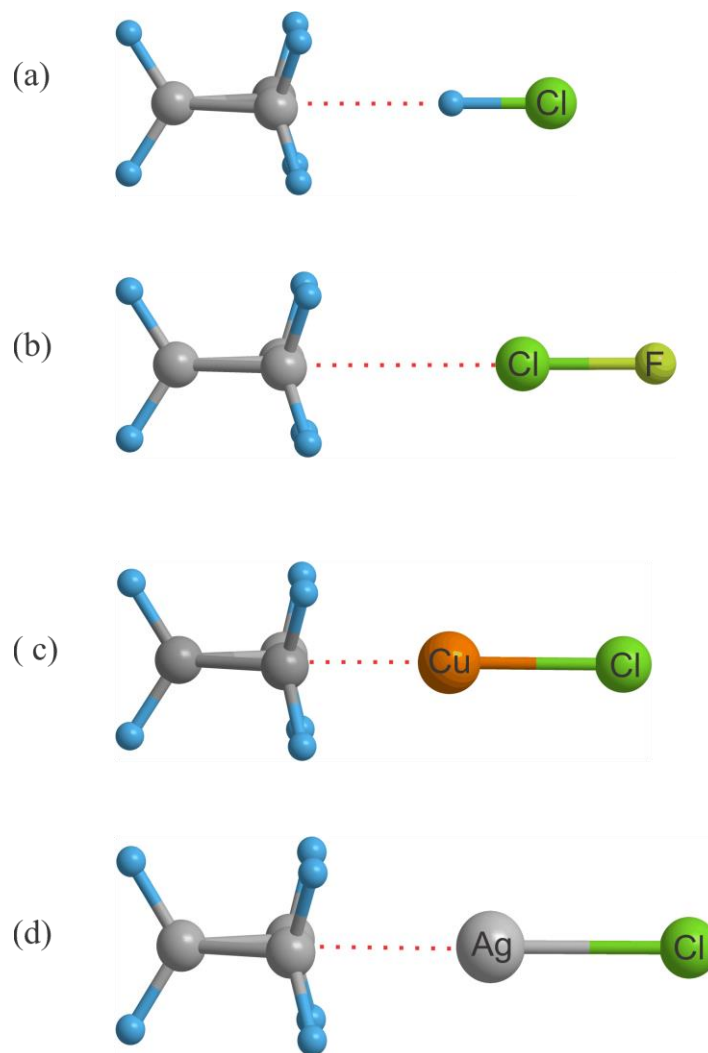


Figure 6. (a)-(d) Observed geometries of $\text{C}_3\text{H}_6 \cdots \text{HCl}$, $\text{C}_3\text{H}_6 \cdots \text{ClF}$, $\text{C}_3\text{H}_6 \cdots \text{CuCl}$ and $\text{C}_3\text{H}_6 \cdots \text{AgCl}$, respectively, drawn to scale.

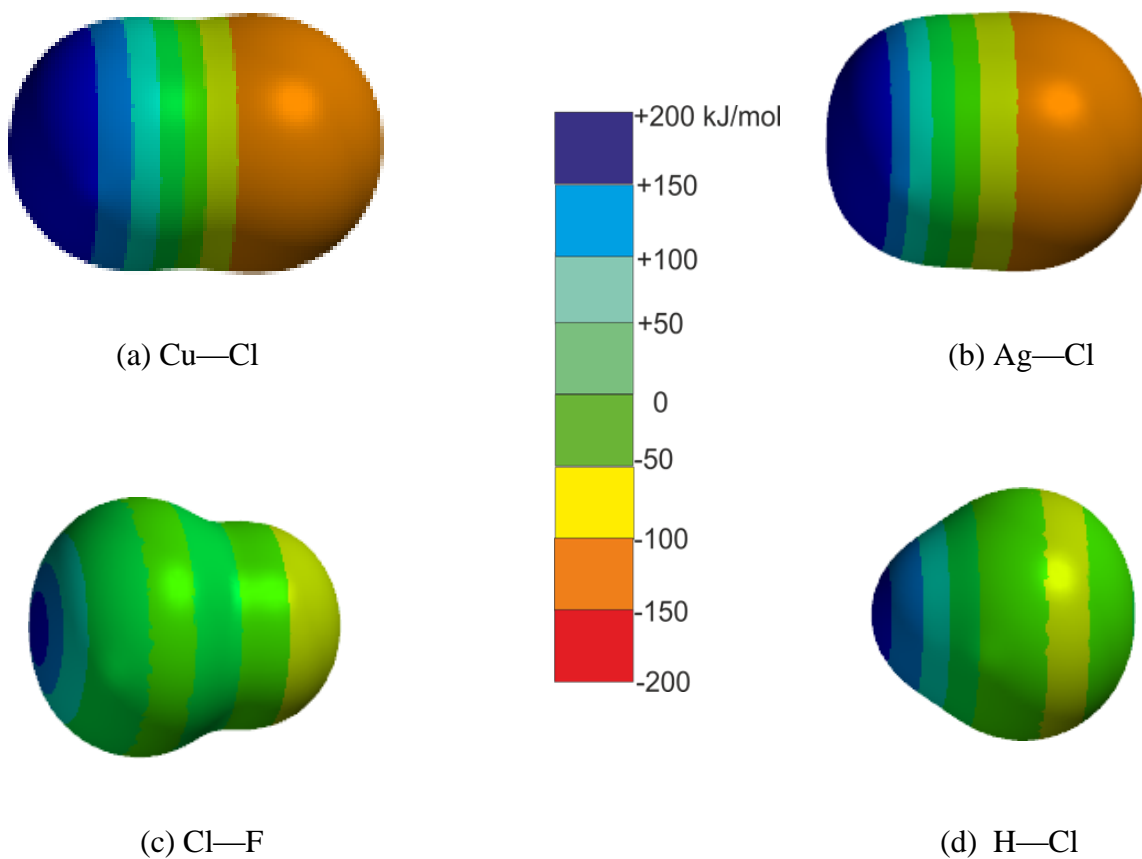


Figure 7. Molecular electrostatic surface potentials (MESP) at the isosurface having an electron density $0.001e/\text{bohr}^3$ for (a) CuCl, (b) AgCl, (c) ClF and (d) HCl. Calculations of these surfaces were carried out with SPARTAN at the M06/6-311G* level for the MCl and the M06/6-311++G** level for ClF and HCl.

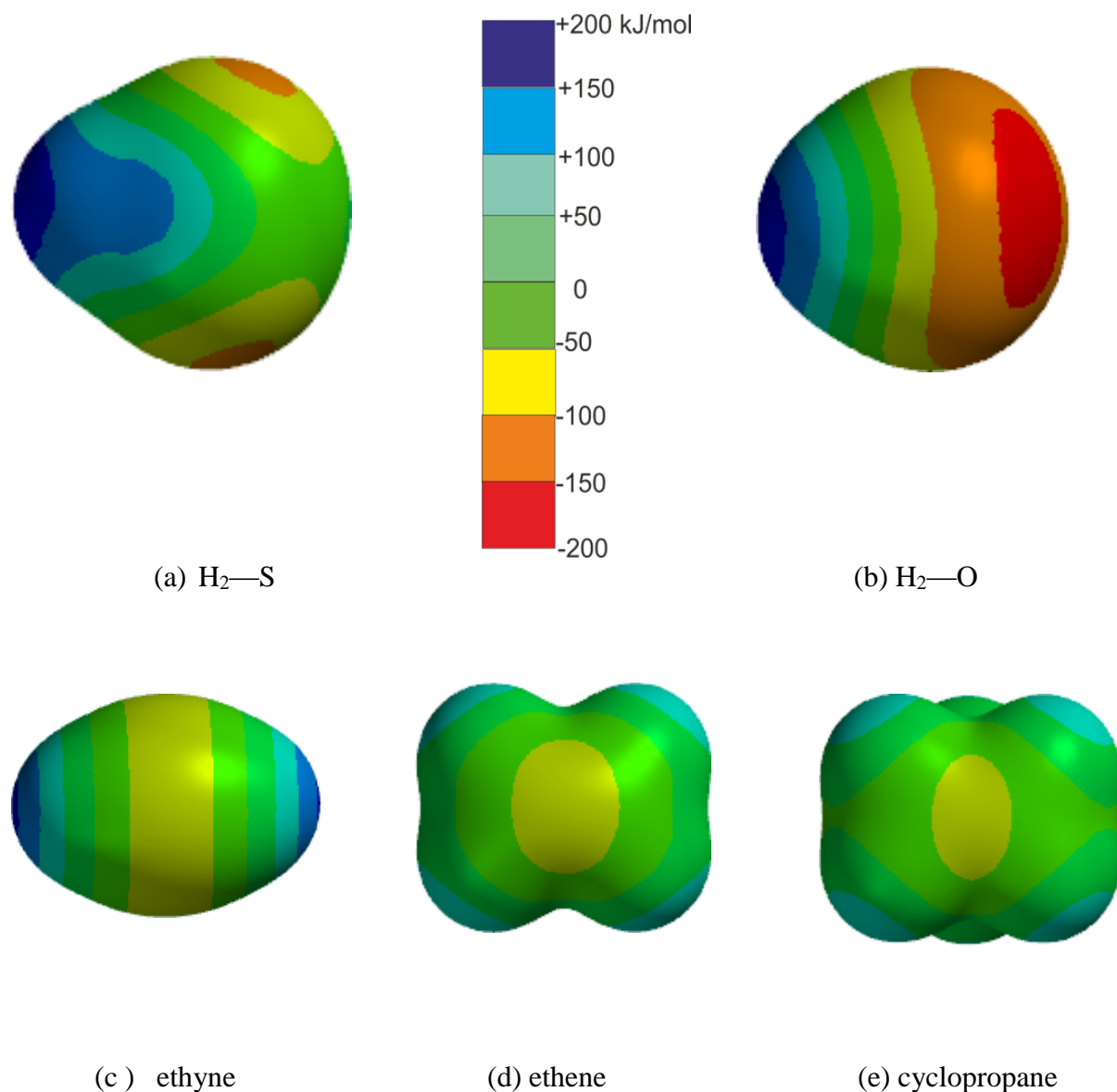


Figure 8. Molecular electrostatic surface potentials (MESP) at the isosurface having an electron density $0.00n \text{ e}/\text{bohr}^3$ for (a) H_2S ($n = 5$), (b) H_2O ($n = 2$), (c) ethyne ($n = 3$), (d) ethene ($n = 3$), and (e) cyclopropane ($n = 3$). Calculations were carried out with SPARTAN at the M06/6-311G++** level. The value of n was chosen to provide suitable contrast. For example, the $0.005 \text{ e}/\text{bohr}^3$ isosurface was used for H_2S the better to show up the (red) n-pair directions. The view shown in (a) and (b) has the plane of the nuclei of each molecule perpendicular to the plane of the paper, i.e. with the two H—S and the two H—O bonds eclipsed. For ethyne and ethene all nuclei lie in the plane of the paper, while for cyclopropane the view is along a C_2 axis from a $\text{CH}_2\text{—CH}_2$ face.